California Environmental Protection Agency

Air Resources Board

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SOP MLD 028

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF SELECTED POLYAROMATIC HYDROCARBONS (PAH) IN AMBIENT AIR

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CALIFORNIA AIR RESOURCES BOARD
MONITORING AND LABORATORY DIVISION

S.O.P. No. MLD 028

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF SELECTED POLYAROMATIC HYDROCARBONS (PAH) IN AMBIENT AIR

1 Scope

This is a high performance liquid chromatographic (HPLC) standard operating procedure for the determination of benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), dibenz[a,h] anthracene (DA), benzo[ghi]perylene (BP), and indeno[1,2,3-cd]pyrene (IP) in the ambient air utilizing a portion of PM10 filters.

2 Summary of Method

2.1 Ambient air is drawn through 8" x 10" PM10 quartz fiber filters at 1.1 M^3/min. for a 24-hour period. Ref the ARB Q/A Manual.

2.2 The PAH's are extracted from a 2" X 5" strip of each filter using 10 % acetonitrile in dichloromethane solvent with sonication. The extract is injected into the HLPC system and identified and quantified by reference to injected external standards with the use of fluorescence detection.

3 Interferences/Limitations

3.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing mis-interpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by running method blanks.

3.2 Interferences co-extracted from the samples will vary considerably from source to source. Individual samples may require a cleanup procedure to achieve the desired sensitivity.

3.3 The chromatographic conditions described have been optimized for the analysis of the six PAHS.

4 Apparatus

4.1 A gradient HPLC system consisting of a mobile phase reservoir, high pressure pumps, an injection valve or automatic sampler, a C-18 reverse phase column, a fluorescence detector and a data system.

4.2 Sampling system: Atmospheric suspended particulate matter is collected on an 8 X 10 inch quartz fiber filter, over a 24 hour period, with a size selective inlet high volume air sampler.

4.3 Culture tubes (50 mL) with teflon lined screw-type caps.

4.4 Ultrasonic bath apparatus, 400 watt output.

4.5 Macro Kuderna-Danish Concentrators such as Supelco #6-4685.

4.6 Amber screw cap vials (4 ml), with teflon lined septum caps, such as Sun Brokers # 1560.

4.7 Whatman O.2 μm syringe PTFE Cat# 6783-1302 filter units, or equivalent.

4.8 Filtration and degassing system for mobile phase solvents such as Waters Part #851234.

4.9 Various volumetric pipets, flasks and graduated cylinders.

4.10 Hotplate.

5 Reagents

5.1 NBS SRM 1647 PAH Reference Solution, is used to calibrate the method. Calibration standards spanning the range of interest are prepared from the stock reference solution.

5.2 PAH Control solutions are purchased from vendors such as Supelco, Inc. The current control solution is Supelco's PAH mix, cat #4-8905.

5.3 Acetonitrile, dichloromethane and water HPLC grade solvents such as Burdick and Jackson products 015, 300 and 365 respectively.

5.4 10 % Acetonitrile in Dichloromethane, UV Grade. Mix 400 mL of UV Grade Acetonitrile with 3600 mL of UV Grade Dichloromethane.

6 Sample Analysis

6.1 Sample Extraction

6.1.1 Cut a 2" x 5" filter paper strip into 1/4 square inch squares and place in a 50 mL screw cap culture tube.

6.1.2 Add 20 mL of 10% ACN/DCM to the culture tube and cap tightly.

6.1.3 Sonicate the culture tube for 30 minutes. Let set for 1 hour, then sonicate for another 30 minutes. Transfer the extract to a 40 ml K-D receiver. Rinse to the extraction flask with an additional 20 ml dichloromethane and evaporate to 2 mL using the K-D concentrator.

6.1.4 Dilute the concentrated extract to 4.0 ml rinsing the K-D receiver sides with acetonitrile. Transfer the sample to an amber screw-capped vial by filtering through a 0.2 micron PTFE filter attached to a 10 ml syringe.

6.1.5 Rinse all glassware thoroughly with acetone and dichloromethane and let drain. Store the extracts in a refrigerator until analysis.

6.1.6 Each batch of extractions must contain a blank filter sample and a "spiked" filter sample (spiked with SRM 1647). These quality control samples must be taken through the same extraction process as used for the samples.

6.2 HPLC Analysis

6.2.1 Operating parameters are as follows:

Column:	Vydax 201TP54 (0.46 x 25 cm)	
Temperature:	28° C ± 0.3°C	
Mobile phase:	50/50 H_2O/ACN to 100 ACN 25 min.	
Detector:	Water's Fluorescence 470	
	Wave Length (λ) nm	
	Excitation	Emission
BbF	290	430
BkF and BaP	297	404
DA and BP	294	392
IP	298	496
Flowrate/Run Time:	1 mL/min; 45 min.	
Retention Time	25 - 35 min	
Inject Volume:	30 μL	

6.2.2 Equilibrate the column for before the first analysis. Analyze a blank to check for method interferences.

6.2.3 Initially, calibrate the instrument using five standard concentrations each analyzed in triplicate. The results are used to prepare a calibration curve. Linear response is indicated when an r of at least 0.98 for a linear least squares fit of the data is obtained.

6.2.4 Check the calibration of the instrument for each analytical run by analyzing 3 standard concentrations and a control standard. The concentration obtained must fall within the UWL and LWL of the control sample value ($\pm$ 2 S.D.). Plot all control analyses on the method control chart. The day to day response for the calibration standards should be within 10%.

6.2.5 Prepare a multi-method routine to control the automatic sampler. Analyze a control and run a sample duplicate every ten analyses. If the detected PAH concentrations fall outside the range to the calibrations standards, the injection volume should be adjusted or the sample diluted, as appropriate and the sample reanalyzed.

7 Calculations

$$ng/M^3 = \frac{(ng/ml)(ml\ of\ extract)(1000)(7)*}{(minutes\ sampled)(SLPM\ air\ flow)}$$

*NOTE: Actual exposed area of 2"x 5" filter strip is 2"x 4.5".

8 Method Sensitivity and Precision

Calibribration Concentration Levels (ng/mL)

	1	2	3	4	5
BbF	4.16	8.32	16.6	33.3	66.6
BkF	4.70	9.40	18.8	37.6	72.5
BaP	4.92	9.84	19.7	39.4	78.7
DA	3.64	7.28	14.6	29.1	58.2
BP	3.76	7.52	15.0	30.1	60.2

IP	4.37	8.74	17.5	35.0	69.9

Percent RSD, Correlation Coefficients, & Calculated LODs

BbF	0.9	1.3	0.3	0.6	.9999	0.01
BkF	0.4	0.6	0.1	0.1	.9999	0.01
BaP	1.0	0.8	0.1	0.1	.9999	0.01
DA	0.8	1.2	0.1	0.3	.9996	0.03
BP	0.8	0.9	0.6	0.5	.9993	0.02
IP	8.1	3.7	1.2	1.2	.9999	0.05

LOD (ng/M^3) = "X" intercept + 3 S.D. of #1 (lowest) Std.

NOTE: All LODs were rounded off to 0.05 ng/M^3